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(54) Title: THERMOPLASTIC ELASTOMER WITH IMPROVED LOW TEMPERATURE PROPERTIES

(57) Abstract: Thermoplastic elastomer composition comprising: a) at least one thermoplastic polyolefin polymer b) at least one dynamically vulcanized rubber in which the quantity of a) is 10-90 % by weight and the quantity of b) is 90-10% by weight relative to the total quantity of thermoplastic polyolefin polymer and rubber and c) 1-250 parts of oil per 100 parts of rubber, in which the oil comprises an isoparaffinic oil.

THERMOPLASTIC ELASTOMER WITH IMPROVED LOW TEMPERATURE PROPERTIES

The invention relates to a thermoplastic elastomer composition comprising:

a) at least one thermoplastic polyolefinic polymer

b) at least one dynamically vulcanized rubber

in which the quantity of a) is 10-90 % by weight and the quantity of b) is 90-10 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber, and

c) 1-250 parts of oil per 100 parts of rubber.

Such thermoplastic elastomer compositions are known from US-A-4311628. The thermoplastic elastomer compositions comprise a blend of a thermoplastic polyolefinic polymer, a dynamically vulcanized rubber and mineral type of extender oil such as aromatic, naphtalenic or paraffinic oil or mixtures thereof. A drawback of the described thermoplastic elastomer compositions is the fact that they have poor low temperature impact properties, especially for high hardness compositions. This poor low temperature impact performance can be ascribed to the presence of the thermoplastic polyolefinic polymer in the thermoplastic elastomer composition. The higher the quantity of thermoplastic polyolefinic polymer the worse the low temperature impact performance.

The object of the present invention is to completely or largely eliminate the stated drawback.

This object is achieved according to the invention by the thermoplastic elastomer composition comprising an isoparaffinic oil.

Surprisingly, it has been found that the thermoplastic elastomer compositions according to the invention show very good low temperature impact properties. A further advantage is that the thermoplastic elastomer compositions show a good UV resistance. Moreover the thermoplastic elastomer compositions have a low fogging value which makes them suitable for use in for example automotive interior applications.

From EP-A-315363 it is known to prepare EPDM compositions comprising a polyalphaolefinic oil. However, EP-A-315363 is silent about the impact resistance of the EPDM compositions and does not mention nor suggest thermoplastic elastomers.

Thermoplastic elastomer compositions which comprise dynamically vulcanized rubber are known per se and are described in general terms in "Handbook of Thermoplastic Elastomers, by B.M. Walker/C.P. Rader, chapter 4, Elastomeric Alloy Thermoplastic Vulcanisates, Van Nostrand Reinhold, New York, 1988".

Suitable thermoplastic polyolefinic polymers in the thermoplastic elastomer composition according to the invention are the thermoplastic polyolefins known per se. Examples of these thermoplastic polyolefins are polyethylene, polypropylene, random or block copolymers of polypropylene, polybutene, polymethylpentene or copolymers of ethylene with alphaolefins such as a copolymer of ethylene and 1-butene or ethylene and 1-octene.

Preferably the thermoplastic elastomer composition comprises polyethylene or polypropylene as thermoplastic polyolefin.

A suitable quantity of the thermoplastic polyolefinic polymer in the thermoplastic elastomer composition according to the invention is between 10-90 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber. Preferably the quantity of the thermoplastic polyolefinic polymer is between 20-85 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber.

Suitable rubbers in the thermoplastic elastomer composition according to the invention are rubbers that can be dynamically vulcanized. During the preparation of the thermoplastic elastomer composition, the rubber and the thermoplastic polyolefinic polymer are heated and mixed, with the rubber being vulcanized. Such vulcanization is referred to as dynamic vulcanization because it takes place during the melt mixing of the thermoplastic elastomer composition. The dynamically vulcanized rubber in the thermoplastic elastomer composition is dispersed in a matrix of the thermoplastic polyolefinic polymer. Examples of suitable rubbers are the following rubbers or a mixture thereof: SBR (styrene-butadiene rubber, copolymer of styrene and butadiene), NBR (nitrile rubber, copolymer of butadiene and acrylonitrile), IIR (butyl rubber, copolymer of isobutene and isoprene) or BR (butadiene rubber). Other examples of suitable rubbers are styrene-containing block copolymers: SBS (Styrene butadiene block copolymer), SEBS (styrene ethylene/butadiene styrene block copolymer), SIPS (styrene isoprene block copolymer).

Yet more examples of suitable rubbers are olefinic rubbers; these are rubbers based on homopolymers and copolymers of polyolefinic polymers. Examples of these are EPDM rubber (copolymer of ethylene, propylene and a third monomer) or a mixture of EPM rubber (copolymer of ethylene and propylene) and EPDM rubber.

Preferably, the dynamically vulcanized rubber in the thermoplastic elastomer composition according to the invention is an olefinic rubber. It is especially preferred for the dynamically vulcanized rubber in the thermoplastic elastomer composition according to the invention to be a copolymer of ethylene, propylene and a third monomer (EPDM) or a mixture of EPDM and a copolymer of ethylene and propylene (EP) or a copolymer of ethylene with a higher alphaolefin or a mixture of EPDM, EP, styrene butadiene block copolymer (SBS) and/or styrene ethylene/butadiene styrene block copolymer (SEBS).

A suitable quantity of the dynamically vulcanized rubber in the thermoplastic elastomer composition according to the invention is between 90-10 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber. Preferably, the quantity of the dynamically vulcanized rubber is between 80-15 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber.

The thermoplastic elastomer composition according to the invention comprises between 1-250 parts of oil per 100 parts of rubber. Preferably the quantity of oil is between 50-200 parts per 100 parts of rubber. It is especially preferred for the thermoplastic elastomer composition to comprise between 100-160 parts of oil per 100 parts of rubber.

Any known isoparaffinic oil may be used in the thermoplastic elastomer composition according to the invention. Isoparaffinic oil is also known as polyalfaolefinic oil which is a colourless, odourless, isoparaffinic, synthetic fluid of high purity composed of hydrogenated oligomers. Polyalfaolefinic oil comprises oligomers of alphaolefins which contain alphaolefin monomer units of at least 3 carbon atoms. Examplary oligomers of alphaolefins contain monomer units with from 6 to 12 carbon atoms. Preferred oligomers of alphaolefins contain monomers with 10 carbon atoms. Preferably, use is made of isoparaffinic oil with a weight-average molecular weight of 1000 g/mole or lower. Isoparaffinic oil with a weight-average molecular weight of between 250 and 700 g/mole is especially preferred. Isoparaffinic oil with a weight-average molecular weight of between 400 and 600

g/mole is even more preferred.

In the thermoplastic elastomer composition according to the invention there may be present, besides the isoparaffinic oil, for example one or more other oils. Suitable oils that may be used in addition to the isoparaffinic oil are for example mineral paraffinic oil, naphthenic oil, aromatic oil or mixtures thereof. Preferably a highly hydrogenated oil is used in which the concentration of aromatic compounds is preferably less than 4 wt.% and the concentration of polar compounds is less than 0.3 wt.%. An example of such oil is PennzUltra (TM) 1199, supplied by Pennzoil in the United States of America. The quantity of isoparaffinic oil in the thermoplastic elastomer composition according to the invention is preferably at least 25 % by weight of the total quantity of oil. More preferably the thermoplastic elastomer composition comprises at least 50 % by weight isoparaffinic oil relative to the total quantity of oil.

In addition, the thermoplastic elastomer composition according to the invention may comprise customary and known additives. Examples of such additives are fillers, reinforcing agents, colourants and stabilizers.

A process for producing the thermoplastic elastomer compositions which comprise dynamically vulcanized rubber is known per se and is described in general terms in US-A-4,311,628. That process is suitable for producing the thermoplastic elastomer composition according to the invention. A suitable process comprises for example mixing and heating the thermoplastic polyolefinic polymer with the rubber, the vulcanising agent and additives, if any, at a temperature above the melting point of the thermoplastic polyolefinic polymer in which the rubber is dynamically vulcanized and the thermoplastic elastomer composition is formed.

The point in time at which the oil that is present in the thermoplastic elastomer composition according to the invention is metered is not critical. In the process, the oil is added for example before or after the dynamic vulcanization of the rubber. It is also possible for the oil to be added partly before and partly after the dynamic vulcanization of the rubber. It is also possible for the rubber used to be pre-mixed with the desired quantity of oil or a proportion thereof.

Suitable vulcanizing agents for the thermoplastic elastomer composition according to the invention are the vulcanizing agents known per se for vulcanizing the stated rubbers. Examples of suitable vulcanizing agents are

phenol resins, peroxide, alkoxysilane and hydrosilane compounds.

The above-mentioned process for producing the thermoplastic elastomer composition according to the invention may be carried out with the aid of items of equipment known per se. Examples of suitable items of equipment are extruders, mixers and kneaders.

The thermoplastic elastomer composition according to the invention may be used in moulded articles which are applied in cars, equipment and constructions. Examples hereof are airbag covers, fuel lines, hoses, dashboard foils, door panels, spoilers, mud flaps, seals, boots, strips and exterior trim.

The invention is elucidated with reference to the following examples, without being limited thereto.

Example I

The following materials were metered to a ZSK40 40-mm twin-screw extruder:

100 parts by weight of EPDM rubber (Keltan© 509 supplied by DSM)
250 parts by weight of polypropylene (Stamylan© P13E10 supplied by DSM)
10 parts by weight of talc (of Sigma-Aldrich)
5 parts by weight of zinc oxide (ZnO supplied by Sigma-Aldrich)
1 part by weight of zinc stearate (supplied by Sigma-Aldrich)
1.5 parts by weight of phenol resin (SP1045 supplied by Schenectady)
1 part by weight of tin(II)chloride ($SnCl_2.2H_2O$ supplied by Alldrich)
1.5 parts by weight of antioxidant (Irganox © 1076 supplied by Ciba Geigy)
140 parts by weight of isoparaffinic oil (Nexbase © 2006 supplied by Neste).

The extruder heating system had been adjusted to a temperature of 205°C. The metered materials were mixed, in which process the EPDM rubber was dynamically vulcanized. Thermoplastic elastomer composition I was obtained in the process.

Test specimens were prepared from thermoplastic elastomer I and their properties were measured according to the test standards stated in Table 1.

Table 1

Property	Test standard
Hardness	DIN 53505
Tensile strength	ISO 37
Modulus 100%	ISO 37
Modulus 300%	ISO 37
Elongation at break	ISO 37
Compression set, 70 h/23°C	ISO 815/B
Compression set, 22 h/70°C	ISO 815/B
Notched Izod -45°C	ISO 180/4 A
Fogging	DIN 75201/B
UV test surface	P.S.A. D47 1431/-G (1992)

The results of the performed tests are shown in Table 3.

Comparative experiment A

The isoparaffinic oil of Example I was replaced by an equal quantity of mineral paraffinic oil, Sunpar©150, from Sun Oil.
The applied quantities of the various components are stated in Table 2.
The properties of thermoplastic elastomer A were determined according to the tests in Table 1. The results are stated in Table 3.

Example II

A proportion of the isoparaffinic oil, 50 parts by weight, of Example I was replaced by an equal quantity of a mineral paraffinic oil, Sunpar©150, from Sun Oil.
The applied quantities of the various components are stated in Table 2.
The properties of thermoplastic elastomer II were determined according to the tests of Table 1. The results are stated in Table 3.

Example III

The oil of example I was replaced by 60 parts by weight of isoparaffinic oil (Nexbase©2004 from Neste) and 100 parts by weight of Sunpar© 150.

The quantity polypropylene was lowered to 40 parts by weight.
The quantity of talc was increased to 30 parts by weight and the quantity of phenol resin was increased to 3.5 parts by weight.
The applied quantities of the various components are stated in Table 2.
The properties of thermoplastic elastomer III were determined according to the tests of Table 1. The results are stated in Table 3.

Table 2

Composition of the examples and comparative experiment A.

Quantities are expressed as parts by weight.

Material	I	A	II	III
Keltan ® 509	100	100	100	100
Stamylan® P13E10	250	250	250	40
Talc	10	10	10	30
ZnO	5	5	5	5
Zinc stearate	1	1	1	1
SP1045	1.5	1.5	1.5	3.5
$SnCl_2.2H_2O$	1	1	1	1
Irganox® 1076	1.5	1.5	1.5	1.5
Nexbase® 2006	140		90	
Nexbase® 2004				60
Sunpar® 150		140	50	100

Table 3. Test results

Test	Unit	I	A	II	III
Hardness	Shore A or Shore D	42 D	43D	43 D	58 A
Tensile strength	MPa	15.0	15.1	15.1	3.8
Modulus 100%	MPa	11.1	11.1	11.0	2.2
Modulus 300%	MPa	11.8	12	11.9	3.9
Elongation at break	%	623	643	604	310
Compression set, 70 h/23°C	%	41	43	42	20
Compression set, 22 h/70°C	%	56	58	58	29
Notched Izod -45°C	-	Tough fracture	Brittle fracture	Tough fracture	Tough fracture
Notched Izod energy	KJ/m2	64	8	56	59
Fogging	mg	1.6	1.5	1.2	1.0
UV test surface	-	No Change	No change	No Change	None Change

Analysis of the test results in Table 3 indicate that thermoplastic elastomer compositions comprising isoparaffinic oil show improved low temperature impact properties in comparison with thermoplastic elastomer compositions comprising only mineral paraffinic oil.

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CLAIMS

1. Thermoplastic elastomer composition comprising:
a) at least one thermoplastic polyolefinic polymer
b) at least one dynamically vulcanized rubber
in which the quantity of a) is 10-90 % by weight and the quantity of b) is 90-10 % by weight relative to the total quantity of thermoplastic polyolefinic polymer and rubber and
c) 1-250 parts of oil per 100 parts of rubber,
characterised in that the thermoplastic elastomer composition comprises an isoparaffinic oil.

2. Thermoplastic elastomer composition according to Claim 1, characterized in that the isoparaffinic oil has a weight average molecular weight of 1000 g/mole or lower.

3. Thermoplastic elastomer composition according to Claim 2, characterized in that the isoparaffinic oil has a weight average molecular weight of between 250 and 700 g/mole.

4. Thermoplastic elastomer composition according to Claim 3, characterized in that the isoparaffinic oil has a weight average molecular weight of between 400 and 600 g/mole.

5. Thermoplastic elastomer composition according to Claim 1, characterized in that the quantity of oil is between 50-200 parts per 100 parts of rubber.

6. Thermoplastic elastomer composition according to Claim 5, characterized in that the quantity of oil is between 100-160 parts per 100 parts of rubber.

7. Thermoplastic elastomer composition according to Claim 1, characterised in that the thermoplastic polyolefinic polymer is polyethylene or polypropylene.

8. Thermoplastic elastomer composition according to Claim 1, characterized in that the dynamically vulcanized rubber is an olefinic rubber.

9. Thermoplastic elastomer composition according to Claim 8, characterized in that the dynamically vulcanized rubber is a copolymer of ethylene, propylene and a third monomer (EPDM) or a mixture of EPDM and a copolymer of ethylene and propylene (EPM) or a copolymer of ethylene with a higher alphaolefin or a mixture of EPDM, EPM, styrene butadiene

block copolymer (SBS) and/or styrene ethylene/butadiene styrene block copolymer (SEBS).

10. Moulded article containing a thermoplastic elastomer composition according to Claims 1-9.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/04 C08L23/10 C08L23/16 C08K5/00 C08L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 44041 A (WICKSTROEM GOERAN ;UPOFLOOR OY (FI); KARTTUNEN MIKKO (FI); PELTONE) 8 October 1998 (1998-10-08) abstract; claims 1-12 page 3, line 31-39 page 5, line 1-8,19-23,35 page 8, line 25 -page 9, line 7 page 13; table 3 ---	1-9
Y	EP 0 742 268 A (ADVANCED ELASTOMER SYSTEMS) 13 November 1996 (1996-11-13) abstract; claims 1-17 page 2, line 50 page 3, line 16,45 page 4, line 1,50 page 5, line 1-5 --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 645 791 A (THEODORE ARES N ET AL) 24 February 1987 (1987-02-24) abstract; claims 1-18 column 2, line 51-53,59-61 column 3, line 19,42,54-67 column 4, line 2-6,15-26 column 5, line 31	1-10

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Ir ional Application No
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